D E C L A R A T I O N

I, Kazuya MINAMISAKA, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true, and faithful translation into English made by me of the of Japanese Patent Application Number 2004-182102.

Signed this 2nd of February, 2009

Kazuya Minamisaka

Kazuya MINAMISAKA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Applicant(s):	Sumitomo Chemical Company, Limited

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Hiroshi OGAWA (SEAL)

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[Name of Material] Specification 1

[Name of Material] Abstract 1

[Number of General Power] 0212949

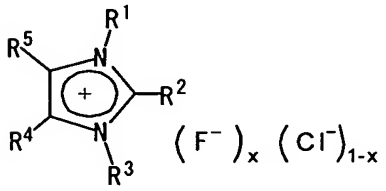
[Necessity for Proof] Yes

[Title of Document] SCOPE OF CLAIMS FOR PATENT

[Claim 1]

A method for producing an alkyl-substituted imdazolium salt containing a fluoride ion represented by the formula (2):

[Formula 2]

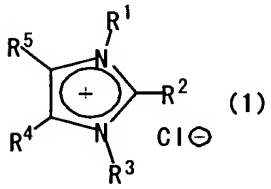


(2)

wherein R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, R^2, R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, and $0<x\leqq 1$,

which comprises reacting an alkyl-substituted imidazolium chloride represented by the formula (1):

[Formula 1]



(1)

wherein R^1, R^2, R^3 , R^4 and R^5 are the same as defined above, with potassium fluoride in methanol.

[Title of Document] SPECIFICATION

[Title of the Invention] Method for producing an alkyl-substituted imidazolium salt containing a fluoride ion

[Technical Field]

[0001]

The present invention relates to a method for producing an alkyl-substituted imidazolium salt containing a fluoride ion.

[Background Art]

[0002]

A alkyl-substituted imidazolium salt containing a fluoride ion is an important compound as a fluorinating agent and an electrolyte raw material. As methods for producing the alkyl-substituted imidazolium fluoride, for example, a method comprising reacting an alkyl-substituted imidazolium chloride with hydrogen fluoride (e.g. Non-patent document 1), a method comprising reacting an alkyl-substituted imidazolium carbonate with ammonium fluoride (e.g. patent document 1) and the like have been known. However, highly corrosive and toxic hydrofluoric acid is used in the former method, and an imidazolium methyl carbonate, which has a problem from the viewpoint of availability, is used as a raw material, and therefore, further improvement has been desired.

[0003]

[Patent document 1] JP 2003-335734 A

[Non-patent document 1] J. Fluorine. Chem., 99, 1 (1999)

[Disclosure of the Invention]

[Problems to be solved by the Invention]

[0004]

Under these circumstances, the present inventor has intensively studied in order to develop more industrially advantageous

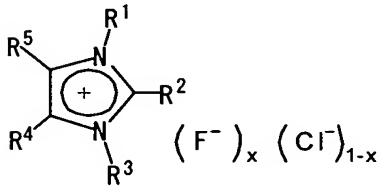
method for producing an alkyl-substituted imidazolium fluoride and, as a result, he has found that an alkyl-substituted imidazolium fluoride can be easily produced by reacting an alkyl-substituted imidazolium chloride with potassium fluoride in methanol, thereby completing the present invention.

[Means for Solving the Problems]

[0005]

That is, the present invention is to provide a method for producing an alkyl-substituted imdazolium salt containing a fluoride ion represented by the formula (2):

[Formula 2]

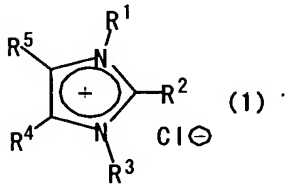


(2)

wherein R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, R^2, R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, and $0<x\leqq 1$,

which comprises reacting an alkyl-substituted imidazolium chloride represented by the formula (1):

[Formula 1]



(1)

wherein R^1, R^2, R^3 , R^4 and R^5 are the same as defined above, with potassium fluoride in methanol.

[Effects of the Invention]

[0006]

According to the present invention, an alkyl-substituted imidazolium salt containing a fluoride ion, which is an important as a fluorinating agent, an electrolyte raw material and the like, can be produced without using highly corrosive and toxic hydrogen fluoride, from an highly available alkyl-substituted imidazolium chloride and potassium fluoride, and therefore, it is useful industrially.

[Best Mode for Carrying out the Invention]

[0007]

The present invention will be illustrated in detail below.

[0008]

In the alkyl-substituted imidazolium chloride represented by the formula (1) (hereinafter, simply referred to as the alkyl-substituted imidazolium chloride (1)), in the formula, R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, and R^2, R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group.

[0009]

Herein, examples of the alkyl group include a straight chain, branched chain or cyclic C1-20 alkyl group such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an n-decyl group, a cyclopropyl group, a 2,2-dimethylcyclopropyl group, a cyclopentyl group, a cyclohexyl group and a menthyl group. The alkyl group may be substituted with a C1-20 alkoxy group which may be substituted such as a methoxy group, an ethoxy group, an n-propoxy group, an isopropoxy group, an n-butoxy group, an isobutoxy group, a sec-butoxy group, a tert-butoxy group

and a trifluoromethoxy group; a C6-20 aryl group which may be substituted such as a phenyl group, a 4-methylphenyl group and 4-methoxyphenyl group; a C6-20 aryloxy group which may be substituted such as a phenoxy group, a 2-methylphenoxy group, a 4-methylphenoxy group, a 4-methoxyphenoxy group and a 3-phenoxyphenoxy group; a C7-20 aralkyloxy group which may be substituted such as a benzyloxy group, a 4-methylbenzyloxy group, a 4-methoxybenzyloxy group and a 3-phenoxybenzyloxy group; a fluorine atom; a C2-20 alkylcarbonyl group which may be substituted such as an acetyl group and an ethylcarbonyl group; a C7-20 arylcarbonyl group which may be substituted such as a benzoyl group, a 2-methylbenzoyl group, a 4-methylbenzoyl group and a 4-methoxybenzoyl group; a C8-20 aralkylcarbonyl group which may be substituted such as a benzylcarbonyl group, a 4-methylbenzylcarbonyl group and a 4-methoxybenzylcarbonyl group; or a carboxyl group. Examples of the alkyl group substituted with the substituent include a fluoromethyl group, a trifluoromethyl group, a methoxymethyl group, an ethoxymethyl group and a methoxyethyl group.

[0010]

Examples of the alkyl-substituted imidazolium chloride (1) include 1,3-dimethylimidazolium chloride,
1,2,3-trimethylimidazolium chloride,
1,2,3,4-tetramethylimidazolium chloride,
1,2,3,4,5-pentamethylimidazolium chloride,
1-methyl-3-ethylimidazolium chloride,
1,2-dimethyl-3-ethylimidazolium chloride, 1,3-diethylimidazolium chloride, 1-methyl-3-n-propylimidazolium chloride,
1-methyl-3-n-butylimidazolium chloride,
1,2-dimethyl-3-n-butylimidazolium chloride,

1-methyl-3-n-pentylimidazolium chloride,
1-methyl-3-n-hexylimidazolium chloride,
1,3-dimethyl-2-ethylimidazolium chloride,
1,3-dimethyl-2-n-propylimidazolium chloride,
1,3-dimethyl-2-n-butylimidazolium chloride,
1-dodecyl-2-methyl-3-dodecylimidazolium chloride,
1-dodecyl-2-methyl-3-benzylimidazolium chloride,
1-ethoxymethyl-3-methylimidazolium chloride and
1-trifluoromethyl-3-methylimidazolium chloride. These may be formed complexes with water, a polar inert solvent or the like.

[0011]

The alkyl-substituted imidazolium chloride (1) can be produced, for example, according to a known method such as a reaction of a substituted imidazole compound and an alkyl chloride (e.g. Tetrahedron, 59, 2253 (2003)).

[0012]

The alkyl-substituted imidazolium salt containing a fluoride ion represented by the formula (29 (hereinafter, simply referred to as the alkyl-substituted imidazolium salt (2)) can be obtained by reacting the alkyl-substituted imidazolium chloride (1) with potassium fluoride in methanol.

[0013]

A commercially available potassium fluoride can be used as it is. The used amount thereof is not particularly limited and the purpose of the present invention is usually accomplished by using about 0.4 to 2 moles thereof.

[0014]

A little amount of water or the other organic solvent may be contained in methanol used in the present invention, and that

in which methanol content is about 90% or more is usually used. The used amount thereof is not particularly limited and it is usually about 100 parts by weight or less.

[0015]

When the reaction temperature is too low, the reaction hardly proceeds and, when the reaction temperature is too high, side reaction such as degradation of the starting material or product may proceed. Therefore, the practical reaction temperature is usually a range of about -20 to 200°C.

[0016]

X in the alkyl-substituted imidazolium salt (2) is a value in a range of $0<x\leqq1$, and the it is decided chiefly by used amounts of potassium fluoride and methanol, water content, the reaction temperature or the like, and therefore, these reaction conditions may be decided accordingly depending on the desired value of x.

[0017]

The mixing order of the reaction agents is not particularly limited and for example, potassium fluoride may be added into a solution containing the alkyl-substituted imidazolium chloride (1) under the condition of the reaction temperature and they may be added in the inverted order. After both agents and the solvent are simultaneously mixed, the reaction temperature may be adjusted.

[0018]

The present reaction may be carried out at normal pressure or under pressure. Alternatively, the progress of the reaction can be checked by a conventional analytical means such as ion chromatography, NMR and IR.

[0019]

After completion of the reaction, potassium chloride formed

in the ion-exchange is usually precipitated in the system. After removing this using a conventional method such as filtration and decantation, the alkyl-substituted imidazolium salt (2) can be obtained by concentrating the obtained solution. When potassium chloride and potassium fluoride remained are precipitated in process of the concentration, the concentration may be carried out again after removing these inorganic salts by the above-mentioned conventional method. The alkyl-substituted imidazolium salt (2) obtained may be further purified, if necessary, by a means such as crystallization and column chromatography.

[0020]

When x is 1, examples of the alkyl-substituted imidazolium salt (2) thus obtained include 1,3-dimethylimidazolium fluoride, 1,2,3-trimethylimidazolium fluoride,
1,2,3,4-tetramethylimidazolium fluoride,
1,2,3,4,5-pentamethylimidazolium fluoride,
1-methyl-3-ethylimidazolium fluoride,
1,2-dimethyl-3-ethylimidazolium fluoride, 1,3-diethylimidazolium fluoride, 1-methyl-3-n-propylimidazolium fluoride,
1-methyl-3-n-butylimidazolium fluoride,
1,2-dimethyl-3-n-butylimidazolium fluoride,
1-methyl-3-n-pentylimidazolium fluoride,
1-methyl-3-n-hexylimidazolium fluoride,
1,3-dimethyl-2-ethylimidazolium fluoride,
1,3-dimethyl-2-n-propylimidazolium fluoride,
1,3-dimethyl-2-n-butylimidazolium fluoride,
1-dodecyl-2-methyl-3-dodecylimidazolium fluoride,
1-dodecyl-2-methyl-3-benzylimidazolium fluoride,
1-ethoxymethyl-3-methylimidazolium fluoride and

1-trifluoromethyl-3-methylimidazolium fluoride.

[0021]

When x satisfies $0<x<1$, examples thereof include an alkyl-substituted imidazolium mixed salt containing a fluoride ion, which consists of a mixed anions of a fluoride ion and a chloride ion, and an alkyl-substituted imidazolium cation such as 1,3-dimethylimidazolium cation, 1,2,3-trimethylimidazolium cation, 1,2,3,4-tetramethylimidazolium cation, 1,2,3,4,5-pentamethylimidazolium cation, 1-methyl-3-ethylimidazolium cation, 1,2-dimethyl-3-ethylimidazolium cation, 1,3-diethylimidazolium cation, 1-methyl-3-(n-propyl)imidazolium cation, 1-methyl-3-(n-butyl)imidazolium cation, 1,2-dimethyl-3-(n-butyl)imidazolium cation, 1-methyl-3-(n-pentyl)imidazolium cation, 1-methyl-3-(n-hexyl)imidazolium cation, 1,3-dimethyl-2-ethylimidazolium cation, 1,3-dimethyl-2-(n-propyl)imidazolium cation, 1,3-dimethyl-2-(n-butyl)imidazolium cation, 1-dodecyl-2-methyl-3-dodecylimidazolium cation, 1-ethoxymethyl-3-methylimidazolium cation, 1-trifluoromethyl-3-methylimidazolium cation and 1-(n-dodecyl)-2-methyl-3-benzylimidazolium cation.

[Example]

[0022]

The present invention will be further illustrated in more detail by Examples. The present invention is not limited to these Examples.

[0023]

Example 1

Into an Erlenmeyer flask, 1.75 g of 1-methyl-3-(n-butyl)imidazolium chloride and 10 g of methanol (moisture content 1% by weight) were charged and dissolved. After 460 mg of potassium fluoride and 10 g of methanol (moisture content 1% by weight) were charged into another Erlenmeyer flask and dissolved, two methanol solutions were mixed at 25°C and the stirring was continued for 30 minutes at the same temperature. The crystalline precipitated after the reaction was filtered and washed with methanol (moisture content 1% by weight). The filtrate and wash liquid obtained were joined and concentrated. A white powder precipitated from the concentrated oil was removed by decantation and then the white powder was washed with small amounts of methanol. The filtrate, the washed liquid and the concentrated oil were joined and concentrated again to obtain 2.10 g of the colorless oil. This oil crystallized by leaving at room temperature. The obtained oil was identified as the salt consisting of the mixed anion consisting of 61 mol% of the fluoride ion and 39 mol% of the chloride ion, and the 1-methyl-3-(n-butyl)imidazolium cation containing 2/3 mole of methanol and 4/3 mole of water from the result of elementary analysis. Yield based on the imidazolium cation: 100%.

[0024]

Elementary analytical value: C: 48.5, H: 10.3, N: 13.7, F: 5.7, Cl: 6.7

Calculated value: C: 49.5, H: 9.8, N: 13.3, F: 5.5, Cl: 6.6

1H-NMR (δ ppm, DMSO-d6, TMS standard): 0.90 (t, 3H), 1.23 (m, 2H), 1.78 (m, 2H), 3.10 (s, Me group of methanol), 3.90 (s, 3H), 4.22 (t, 2H), 7.85 (d, 2H), 8.5 (bs, 1H)

[0025]

Example 2

Into an Erlenmeyer flask, 8.20 g of 1-methyl-3-(n-butyl)imidazolium chloride and 50 g of methanol (moisture content 1% by weight) were charged and dissolved. After 1.4 g of potassium fluoride and 35 g of methanol (moisture content 1% by weight) were charged into another Erlenmeyer flask and dissolved, two methanol solutions were mixed at 25°C and the stirring was continued for 30 minutes at the same temperature. The crystalline precipitated after the reaction was filtered and washed with methanol (moisture content 1% by weight). The filtrate and wash liquid obtained were joined and concentrated. A white powder precipitated from the concentrated oil was removed by decantation and then the white powder was washed with a small amount of methanol. The filtrate, the washed liquid and the concentrated oil were joined and concentrated again to obtain 9.61 g of the colorless oil. This oil crystallized by leaving at room temperature. The obtained oil was identified as the salt consisting of the mixed anion consisting of 47 mol% of the fluoride ion and 53 mol% of the chloride ion, and the 1-methyl-3-(n-butyl)imidazolium cation containing 2/3 mole of methanol and 1 mole of water from the result of elementary analysis. Yield based on the imidazolium cation: 100%.

[0026]

Elementary analytical value: C: 49.5, H: 10.1, N: 14.0, F: 4.5, Cl: 9.6

Calculated value: C: 50.4, H: 9.6, N: 13.6, F: 4.3, Cl: 9.1

1H-NMR (δ ppm, DMSO-d6, TMS standard): 0.90 (t, 3H), 1.23 (m, 2H), 1.78 (m, 2H), 3.10 (s, Me group of methanol), 3.90 (s, 3H), 4.21 (t, 2H), 7.90 (d, 2H), 8.5 (bs, 1H)

[0027]

Reference Example (Example of use of the alkyl-substituted imidazolium fluoride (2) as a fluorinating agent)

Into a 50 mL flask equipped with a reflux condenser, 430 mg of 1-methyl-3-(n-butyl)imidazolium fluoride obtained in Example 1 and 127 mg of benzyl chloride were charged and the resulting mixture was stirred for 3 hours at 80°C. After cooling to room temperature, 5 g of ethyl acetate was added thereto and stirred. The mixture was separated to two layers by standing. The upper layer was analyzed by gas chromatography (internal standard method) to find out that the main product was benzyl fluoride. Yield: 95%.

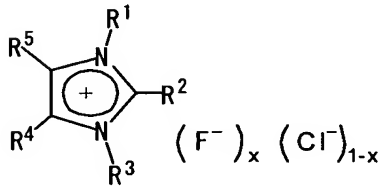
[Title of Document] ABSTRACT

[Abstract]

[Problem] It is to provide an industrially advantageous method for producing an alkyl-substituted imidazolium fluoride.

[Means to Solve] A method for producing an alkyl-substituted imdazolium salt containing a fluoride ion represented by the formula (2):

[Formula 2]

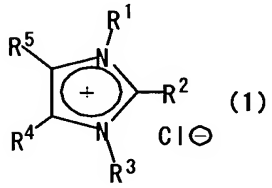


(2)

wherein R^1 and R^3 are the same or different, and each represents an optionally substituted alkyl group, R^2, R^4 and R^5 are the same or different, and each represents a hydrogen atom or an optionally substituted alkyl group, and $0<x\leqq 1$,

which comprises reacting an alkyl-substituted imidazolium chloride represented by the formula (1):

[Formula 1]



(1)

wherein R^1, R^2, R^3 , R^4 and R^5 are the same as defined above, with potassium fluoride in methanol.

[Selected Figure] None

Applicant History Information

Identification No.: [000002093]

1. Changing Date: August 28, 1990

[Reason for changing] Newly registration

Address: 5-33, Kitahama 4-Chome, Chuo-ku,
Osaka-shi, Osaka-fu

Name: Sumitomo Chemical Company, Limited

2. Changing Date: October 1, 2004

[Reason for changing] Name changing
Address changing

Address: 27-1, Shinkawa 2-Chome, Chuo-ku, Tokyo

Name: Sumitomo Chemical Company, Limited